(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 277 847 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.01.2003 Bulletin 2003/04

(51) Int Cl.[7]: **C22C 38/00**, C22C 38/02, C22C 38/04, C23C 8/26

(21) Application number: 02015081.9

(22) Date of filing: 05.07.2002

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR**
Designated Extension States:
**AL LT LV MK RO SI**

(30) Priority: **17.07.2001 JP 2001216990**
**19.03.2002 JP 2002075624**

(71) Applicant: **NISSAN MOTOR COMPANY, LIMITED**
**Yokohama-shi, Kanagawa 221-0023 (JP)**

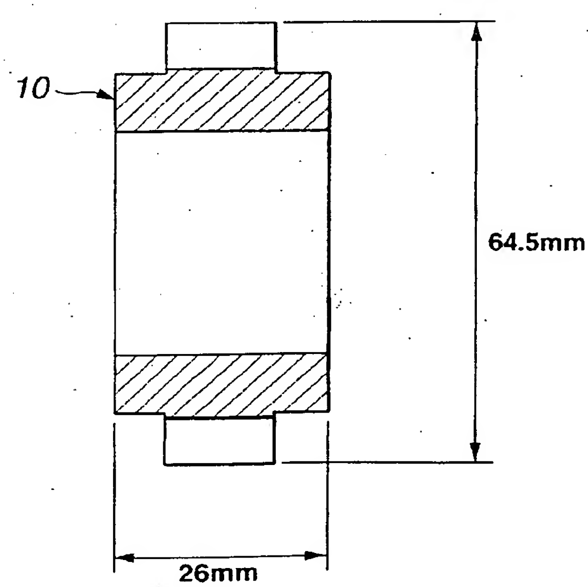
(72) Inventors:
- **Hanyuda, Tomoki**
  **Minami-ku, Nagoya-shi, Aichi 457-0811 (JP)**
- **Nakamura, Tuyoshi**
  **Minami-ku, Nagoya-shi, Aichi 457-0811 (JP)**
- **Hayashi, Takao**
  **Atsugi-shi, Kanagawa 243-0035 (JP)**
- **Usuki, Hideki**
  **Koza-gun, Kanagawa 253-0111 (JP)**
- **Honda, Masatoshi**
  **Minami-ku, Nagoya-shi, Aichi 457-0811 (JP)**
- **Kurebayashi, Yutaka**
  **Minami-ku, Nagoya-shi, Aichi 457-0811 (JP)**
- **Miura, Naomi**
  **Isehara-shi, Kanagawa 259-1117 (JP)**
- **Murakami, Youichi**
  **Yokohama-shi, Kanagawa 232-0066 (JP)**

(74) Representative: **Weber, Joachim, Dr.**
**Hoefer, Schmitz, Weber & Partner**
**Patentanwälte**
**Gabriel-Max-Strasse 29**
**81545 München (DE)**

# (54) Case hardening steel and carburized part using same

(57) A case hardening steel high in impact strength, consists essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of from more than 0.3 to 1.0 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, molybdenum in an amount of not more than 1.0 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, and balance being iron and inevitable impurities. The case hardening steel meets an equation of $[C \%] + 5([P \%] + [S \%]) \leq ([Mn \%] + [Mo \%] + 1.8) / 8$.

FIG.1




EP 1 277 847 A1

Printed by Jouve, 75001 PARIS (FR)

## Description

### BACKGROUND OF THE INVENTION

**[0001]** This invention relates to improvements in a case hardening steel and a carburized part using the case hardening steel, and more particularly to the case hardening steel and carburized part belonging to ferrous material to be used structural parts and to be used for parts required to be high in hardness at their surface layer upon being subjected at their surface layer to a case hardening treatment such as carburizing, carbonitriding and the like (including gas carburizing, solid carburizing, liquid carburizing, salt bath carburizing, plasma carburizing, vacuum carburizing and the like), the parts including engine parts (such as piston pin), gears, shafts and the like sued in engines, transmissions, differentials and the like of an automotive vehicle.

**[0002]** Hitherto, case hardening steels have been known and identified as SCr420H, SCM420H and SNCM420H according to JIS (Japanese Industrial Standard). However, recently it has been eagerly required to improve impact strength of parts for power transmission to meet an increase in power output and weight-lightening made in transportation machines such as automotive vehicles or the like. Accordingly, the above case hardening steels according to JIS seem to be insufficient in impact strength.

**[0003]** In order to meet such a requirement, a method of producing a bevel gear high in impact strength by improving forging and heat treatment manners has been proposed as disclosed in Japanese Patent Provisional Publication No. 9-201644. However, this method has encountered difficulties in which material cost and processing cost are high. Additionally, the impact strength of the bevel gear cannot be largely improved.

### SUMMARY OF THE INVENTION

**[0004]** It is an object of the present invention to provide an improved case hardening steel which can overcome drawbacks encountered in conventional case hardening steels.

**[0005]** Another object of the present invention is to provide an improved case hardening steel which is high in impact strength without causing a large increase in material cost and processing cost as compared with conventional case hardening steels, and a carburized part using the improved case hardening steel.

**[0006]** As a result of eager studies of the present inventors, it has been found to overcome the above problems encountered in the conventional case hardening steels by controlling amounts of elements of C, Mn, Mo, P and S inherently contained in case hardening steel and of B and the like within specified content ranges thereby establishing a suitable balance between crystal grain size and a carburized case (hardened layer).

**[0007]** A first aspect of the present invention resides in a case hardening steel consisting essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of from more than 0.3 to 1.0 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, molybdenum in an amount of not more than 1.0 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, and balance being iron and inevitable impurities. The case hardening steel meets the following equation:

$$[C\,\%] + 5([P\,\%] + [S\,\%]) \leq ([Mn\,\%] + [Mo\,\%] + 1.8) / 8 \qquad \text{Eq. (1).}$$

**[0008]** A second aspect of the present invention resides in a case hardening steel consisting essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of from more than 0.3 to 1.0 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, chromium in an amount of from more than 0 to 1.6 % by weight, and balance being iron (Fe) and inevitable impurities. The case hardening steel meets the following equation:

$$[C\,\%] + 5([P\,\%] + [S\,\%]) \leq ([Mn\,\%] + 1.8) / 8 \qquad \text{Eq. (2).}$$

**[0009]** A third aspect of the present invention resides in a case hardening steel consisting essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of not more than 0.3 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, molybdenum in an amount of not more than 1.0 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, and balance being iron and inevitable impurities. The case hardening steel meets the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + [Mo\ \%] + 1.8) / 8 \quad \text{Eq. (1).}$$

**[0010]** A fourth aspect of the present invention resides in a case hardening steel consisting essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of not more than 0.3 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, and balance being iron and inevitable impurities. The case hardening steel meets the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + 1.8) / 8 \quad \text{Eq. (2).}$$

**[0011]** A fifth aspect of the present invention resides in a carburized part formed of a case hardening steel which consists essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of from more than 0.3 to 1.0 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, molybdenum in an amount of not more than 1.0 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, and balance being iron and inevitable impurities. The case hardening steel meets the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + [Mo\ \%] + 1.8) / 8 \quad \text{Eq. (1).}$$

Additionally, the carburized part has a hardened layer of carburized case including fine austenite whose austenite grain size number according to JIS G 0551 is not smaller than 7.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0012]**

Fig. 1 is a cross-sectional view of a gear specimen used in Experiment 1 for evaluating performance of case hardening steels according to the present invention;
Fig. 2 is a graphic representation showing a heating pattern for carburizing hardening and tempering for obtaining the gear specimen of Fig. 1;
Fig. 3 is a plan view illustrating an impact test by using a drop impact tester, in Experiment 1;
Fig. 4 is a graph showing the relationship between the impact torque (Nm) and the frequency (times) of application of impact load, in connection with the impact test in Experiment 1;
Fig. 5A is a cross-sectional view of an example of a gear specimen used in the impact test in Experiment 2;
Fig. 5B is a cross-sectional view similar to Fig. 5A but showing another example of the gear specimen;
Fig. 6 is a graph showing the relationship between the (cold) forging load ratio and the hardness upon undergoing the spheroidizing annealing, for the steels of Examples and Comparative Examples in connection with Experiment 2; and
Fig. 7 is a graph showing the relationship between the (100 times) impact strength ratio and the value of [(left side) - (right side) of Eq. (1)], for the steels of Examples and Comparative Examples in connection with Experiment 2.

## DETAILED DESCRIPTION OF THE INVENTION

**[0013]** The present invention is based on the present inventors' findings that, in order to improve impact strength of a case hardening steel, it is effective to control the amounts of elements of C, Mn, Mo, P and S inherently contained in the case hardening steel and of B and the like within specified content ranges thereby establishing a suitable balance between crystal grain size and a carburized case (hardened layer) corresponding to an effective case depth. In other words, the present invention depends on the present inventors' knowledge that the impact strength of case hardening steel can be improved upon strong contribution of decreasing the amount of P and S as impurity elements in place of addition of a large amount of Mo and the like which are high in cost, addition of Mn in place of Mo, addition of B, and refining crystal grain.

**[0014]** A first embodiment of a case hardening steel according to the present invention consists essentially of carbon (C) in an amount of from 0.1 to 0.3 % by weight, silicon (Si) in an amount of from more than 0.3 to 1.0 % by weight,

manganese (Mn) in an amount of from 0.3 to 1.7 % by weight, phosphorus (P) in an amount of not more than 0.03 % by weight, sulfur (S) in an amount of not more than 0.03 % by weight, molybdenum (Mo) in an amount of not more than 1.0 % by weight, aluminum (Al) in an amount of not more than 0.04 % by weight, nitrogen (N) in an amount of not more than 0.03 % by weight, and balance being iron (Fe) and inevitable impurities. Additionally, the case hardening steel is prepared to meet the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + [Mo\ \%] + 1.8) / 8 \qquad \text{Eq. (1).}$$

**[0015]** Here, C of component elements of the case hardening steel functions to increase the hardness of the case hardening steel obtained after carburizing hardening and to increase the strength of a carburized (component) part. The content of C is within a range of from 0.1 to 0.3 % by weight. If the content of C is smaller than 0.1 % by weight, the effect of addition of C is insufficient. If the content of C exceeds 0.3 % by weight, the resultant case hardening steel is lowered in toughness and impact strength.

**[0016]** Si promotes intergranular oxidation after carburizing and may lower the strength of the resultant case hardening steel, and therefore it is preferable that the case hardening steel contains not more than 0.3 % by weight of Si. However, the content of Si may not be limited to not more than 0.3 % in a heat treatment such as vacuum carburizing or a plasma carburizing which can suppress the intergranular oxidation. It is to be noted that an excessive content of Si largely degrades machinability and cold forgeability of the case hardening steel, and therefore the upper limit of the Si content is set at 1.0 % by weight.

**[0017]** Mn is an element which is effective for improving hardenability of the case hardening steel. The lower limit of the Mn content is set at 0.3 % by weight for the reason why austenite in a suitable amount is necessary to be retained after carburizing in order to improve the toughness of the case hardening steel. An excessive Mn content over 1.7 % by weight lowers the cold forgeability of the case hardening steel and promotes the intergranular oxidation after the carburizing.

**[0018]** P is an element which functions to lower the toughness of a carburized case (hardened layer) of the case hardening steel. Particularly in case that the content of P exceeds 0.03 % by weight, lowering in impact strength of the case hardening steel becomes conspicuous. Additionally, P is an impurity element, and therefore it is preferable that the P content approaches 0 % by weight as much as possible.

**[0019]** S is an elelment which also functions to lower the toughness of the carburized case (hardened layer). Similarly to P, if the content of S exceeds, lowering in impact strength of the case hardening steel becomes conspicuous. Additionally, S is also an impurity element, and therefore it is preferable that the S content approaches O % by weight as much as possible.

**[0020]** Mo is an element which is effective for improving the hardenability of the case hardening steel and effective for improving the toughness of the carburized case (hardened layer). The Mo content is excessive so as to exceed 1.0 % by weight, such effects become saturated.

**[0021]** Al reacts with N in the case hardening steel to form AlN thereby being effective to prevent coarsening of austenite grain size during carburizing. If the Al content exceeds 0.04 % by weight, the effect of preventing the grain size coarsening becomes saturated. Additionally, for the similar reason, the content of N exceeds 0.03 % by weight, the effect of preventing the grain size coarsening becomes saturated.

**[0022]** It will be understood that Fe occupies an almost whole part of the case hardening steel of the present invention, other than the above-discussed components (elements). The case hardening steel of the present invention further contains Cu, O and the like as inevitable impurities.

**[0023]** The above equation Eq. (1) is a formula for optimizing the contents of C, P, S, Mn and Mo in the case hardening steel in order to suppress formation and propagation of crack at crystal boundary which crack serves as a starting point of breaking. In other words, the toughness of the carburized case (hardened layer) obtained after carburizing can be increased by addition of suitable amounts of Mn and Mo, while the toughness of the crystal boundary can be increased by reducing the contents of P and S as the impurities, so that the case hardening steel can be improved in impact strength.

**[0024]** A second embodiment of a case hardening steel according to the present invention consists essentially of carbon (C) in an amount of from 0.1 to 0.3 % by weight, silicon (Si) in an amount of from more than 0.3 to 1.0 % by weight, manganese (Mn) in an amount of from 0.3 to 1.7 % by weight, phosphorus (P) in an amount of not more than 0.03 % by weight, sulfur (S) in an amount of not more than 0.03 % by weight, aluminum (Al) in an amount of not more than 0.04 % by weight, nitrogen (N) in an amount of not more than 0.03 % by weight, optionally chromium in an amount of from more than 0 to 1.6 % by weight, and balance being iron (Fe) and inevitable impurities. Additionally, the case hardening steel is prepared to meet the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + 1.8) / 8 \qquad \text{Eq. (2).}$$

**[0025]** The case hardening steel of this embodiment is similar in composition and in effects to be produced, to that of the first embodiment with the exception that Mo is not contained. In this embodiment, Mn is added in place of Mo thereby omitting use of Mo which is high in cost. Additionally, the case hardening steel of this embodiment may contain not more than 1.6 % by weight of Cr. Cr is an element which is effective for improving the hardenability of the case hardening steel. However, addition of an excessive amount of Cr may invite embrittlement of crystal grain boundary, and therefore the Cr content is preferably not more than 1.6 % by weight. The lower limit of the Cr content is decided in accordance with a required hardenability and therefore is not particularly set.

**[0026]** Next, a third embodiment of the case hardening steel according to the present invention will be discussed. This case hardening steel consists essentially of carbon (C) in an amount of from 0.1 to 0.3 % by weight, silicon (Si) in an amount of not more than 0.3 % by weight, manganese (Mn) in an amount of from 0.3 to 1.7 % by weight, phosphorus (P) in an amount of not more than 0.03 % by weight, sulfur (S) in an amount of not more than 0.03 % by weight, molybdenum (Mo) in an amount of not more than 1.0 % by weight, aluminum (Al) in an amount of not more than 0.04 % by weight, nitrogen (N) in an amount of not more than 0.03 % by weight, and balance being iron (Fe) and inevitable impurities. Additionally, the case hardening steel is prepared to meet the above equation Eq. (1).

**[0027]** Thus, the case hardening steel of the third embodiment is similar to the case hardening steel of the first embodiment with the exception that the Si content is not more than 0.3 % by weight. Si is an element which is effective for improving the hardenability of the case hardening steel; however, addition of an excessive amount of Si promotes intergranular oxidation after carburizing thereby inviting lowering in strength of the case hardening steel. Accordingly, the Si content is limited to not more than 0.3 % by weight.

**[0028]** Next, a fourth embodiment of the case hardening steel according to the present invention will be discussed. This case hardening steel consists essentially of carbon (C) in an amount of from 0.1 to 0.3 % by weight, silicon (Si) in an amount of not more than 0.3 % by weight, manganese (Mn) in an amount of from 0.3 to 1.7 % by weight, phosphorus (P) in an amount of not more than 0.03 % by weight, sulfur (S) in an amount of not more than 0.03 % by weight, aluminum (Al) in an amount of not more than 0.04 % by weight, nitrogen (N) in an amount of not more than 0.03 % by weight, and balance being iron (Fe) and inevitable impurities. Additionally, the case hardening steel is prepared to meet the above equation of Eq. (2). Thus, the case hardening steel of this embodiment is the same as that of the second embodiment with the exception that the Si content is not more than 0.3 % by weight and no Cr is contained.

**[0029]** The above case hardening steels of the third and fourth embodiments may contain not more than 1.6 % by weight of Cr. Cr is an element which is effective for improving the hardenability of the case hardening steel. However, addition of an excessive amount of Cr may invite embrittlement of crystal grain boundary, and therefore the Cr content is preferably not more than 1.6 % by weight. The lower limit of the Cr content is decided in accordance with a required hardenability and therefore is not particularly set.

**[0030]** Preferably, the above case hardening steels of the third and fourth embodiments have an elemental composition to meet the following equation:

$$80\,[Si\ \%] + 24\,[Mn\ \%] + 33\,[Mo\ \%] + 13 \leq 40 \qquad \text{Eq. (4)}$$

**[0031]** With this elemental composition, the hardness of the material (case hardening steel) before cold forging can be lowered thereby making it possible to lower deformation resistance and improve deformability of the material and additionally to lower a pressing load (or cold forging load) during cold forging. In other words, cold forgeability of the case hardening steel can be improved by preparing the case hardening steel to meet the above equation Eq. (4).

**[0032]** The case hardening steels of the first to fourth embodiments may contain boron (B) in an amount of from 0.001 to 0.005 % by weight, niobium (Nb) in an amount of from 0.01 to 0.10 % by weight and/or titanium (Ti) in an amount of from 0.01 to 0.10 % by weight. The above-mentioned B is an element which is effective for improving the hardenability of the case hardening steel, and also effective for strengthening grain boundary of the carburized case (hardened layer) upon its segregation at the grain boundary of the carburized case (hardened layer). In order to obtain such effects, addition of not less than 0.001 % by weight of B is preferable. However, addition of B in an amount exceeding 0.005 % by weight is not preferable because not only the effect of improving hardenability becomes saturated but also hot or cold machinability is degraded.

**[0033]** It will be understood that at least one of the above-mentioned Nb and Ti may be contained in the case hardening steel. In case that the case hardening steel contains both Nb and Ti, each of Nb and Ti is preferably contained in an amount of from 0.01 to 0.10 % by weight. Nb and Ti react with C and N to form carbide and nitride thereby preventing coarsening of austenite crystal grain. If the content of Nb or Ti is less than 0.01 % by weight, it is difficult to obtain a sufficient effect of preventing the crystal grain coarsening. If the content of Nb or Ti exceeds 0.10 % by

weight, the effect of preventing the crystal grain coarsening becomes saturated.

**[0034]** It is preferable that the case hardening steels of the first to fourth embodiments have an elemental composition to meet the following equation:

$$[C\ \%] + 5.2\ ([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + [Mo\ \%] + 3.8) / 22 + 96\ [B\ \%] + [\text{austenite grain size number according to JIS G 0551}] / 111 \qquad \text{Eq. (3)}$$

**[0035]** With this elemental composition, impurities at crystal grain boundary can be removed under the effect of addition of B, thereby achieving strengthening the grain boundary. Additionally, crystal grain size becomes small, thereby suppressing breaking at crystal grain boundary.

**[0036]** Particularly in case of meeting the above equations Eq. (1) and Eq. (3), achievement can be made on optimizing the contents of C, P, S, Mn and Mo for suppressing the formation and propagation of crack at crystal grain boundary which crack serves as the breaking starting point, and on reinforcement of crystal grain boundary under the effects of addition of B and crystal grain refining. In other words, addition of a suitable amount of Mn and Mo is preferable to improve the toughness of the carburized case (hardened layer) after carburizing, and decreasing the contents of P and S as impurities is preferable to improve the toughness of crystal grain boundary. These concepts lead to the limitation of the equation Eq. (1). It is preferable that impurities at crystal grain boundary are removed under the effect of addition of B thereby to achieve strengthening of grain boundary. Additionally, it is also preferable that crystal grain size is lowered thereby preventing breaking at grain boundary. These concepts lead to the limitation of the equation Eq. (3).

**[0037]** Furthermore, the case hardening steels of the embodiments 1 to 4 may contain lead (Pb) in an amount of not more than 0.3 % by weight, bismuth (Bi) in an amount of not more than 0.15 % by weight and/or calcium (Ca) in an amount of not more than 0.1 % by weight. Pb, Bi and Ca may be contained in any combinations. These elements are effective for improving machinability of the case hardening steel; however, not only the machinability improving effect may become saturated but also the toughness may lower if the Pb content exceeds 0.3 % by weight, the Bi content exceeds 0.15 % by weight or the Ca content exceeds 0.1 % by weight.

**[0038]** A carburized (component) part according to the present invention will be discussed. The carburized part is formed of the above-mentioned case hardening steel and has a carburized case (hardened layer) includes fine austenite whose austenite grain size number according to JIS (Japanese Industrial Standard) G 0551 is not smaller than 7. Such refining crystal grain size is accomplished during carburizing and effective for improving resistance to the crack propagation upon input of impact. If austenite in the carburized case is not so refined that the austenite grain size number is smaller than 7, the carburized part cannot obtain an excellent impact strength characteristics.

**[0039]** Thus, the case hardening steel of the present invention is used as parts whose surface layer requires a.high hardness, such as gears, shafts and the like in a transmission, a differential and the like of an automotive vehicle.

## EXAMPLES

**[0040]** The present invention will be more readily understood with reference to the following Examples in comparison with Comparative Examples; however, these Examples are intended to illustrate the invention and are not to be construed to limit the scope of the invention. Additionally, although the case hardening steels of Examples and Comparative Examples are directed to gears, it will be understood that the principle of the present invention are not limited to gears and therefore may be applied to all machine structural parts which particularly regard impact strength characteristics as important.

## EXPERIMENT 1

**[0041]** Steels A to I, K to M and R of Examples (according to the present invention) and steels N to Q of Comparative Examples (not according to the present invention) in an amount of 150 Kg were produced in a usual manner under vacuum melting. The steels A to R and the steels N to Q had chemical compositions shown in Table 1. The steel N of Comparative Example corresponded to a conventional case hardening steel identified as SCr420H according to JIS. Subsequently, each of these steels was subjected to rolling and normalizing in a usual manner, and thereafter was machined to a gear shape having a module of 1.5 as shown in Fig. 1. The gear shaped steel had an outer diameter (corresponding to addendum circle) of 64.5 mm and a width (axial dimension) of 26 mm as illustrated in Fig. 1. Thereafter, each gear shaped steel was subjected to carburizing hardening and tempering in a heating pattern as shown in Fig. 2, followed by finish machining, thereby obtaining gear specimen 10 shown in Fig. 1.

**[0042]** An impact test was conducted on each gear specimen 10 by using a drop impact tester as shown in Fig. 3.

With the impact tester, gear specimen 10 was fixedly mounted on a first shaft and engaged with opposed gear 12 fixedly mounted on a second shaft supported by a supporting base 14. A torque arm 16 has a base end section fixedly mounted on the first shaft. A free end section of the torque arm 16 has a position 18 to which impact load was repeatedly applied so as to apply impact (load) torque (Nm) to gear specimen 10. In this impact test, the frequency or number (times) of application of the impact load to torque arm 16 at a time when breaking of the gear specimen 10 had occurred was measured. This measurement of the frequency of impact load application was made plural times by changing the impact torque to be applied to the gear specimen, thereby obtaining an upper group of data for each gear specimen of Example and a lower group of data for each gear specimen of Comparative Example. In the upper group of data, each black dot indicates the measured frequency of impact load application at a value of the impact torque. In the lower linear data, each light triangle indicated the measured frequency of impact load application at a value of the impact torque.

**[0043]** From each of the upper group of data and the lower group of data in Fig. 4, an impact (load) torque (Nm) applied to the gear specimen in case that the (measured) frequency of impact load application was 100 times (at which the gear specimen was broken) was determined from a relational expression between the impact torque and the frequency of impact load application, i.e. in a manner using a dotted arrow as illustrated in Fig. 4. The dotted arrow is drawn from a straight line representing the upper or lower group of data. The thus determined impact torque is referred to as "100 times impact strength (Nm)". The 100 times impact strength for each of the gear specimens of Examples and Comparative Examples is shown in Table 2.

**[0044]** Additionally, austenite grain size of the gear specimens of Examples and Comparative Examples were determined by a judgment method using crossover line segments, according to JIS G 0551. The thus determined austenite grain size of the gear specimens are shown in Table 2.

**[0045]** As apparent from the experimental results shown in Table 2, the gear specimens formed of the steels A to I, K to M and R of Examples meet either one of the above equations Eq. (1) and Eq. (2) and the equation Eq. (3) by optimizing balance between the impurity elements and the added elements, and therefore are high in impact strength as compared with those formed of the steels of Comparative Example. In contrast, the gear specimen formed of the steel N of Comparative Example cannot meet the above equations Eq. (2) and Eq. (3) and therefore are low in impact strength. The gear specimen formed of the steel O of Comparative Example contains much Cr and cannot meet the above equations Eq. (2) and Eq. (3), and therefore is low in impact strength. The gear specimen formed of the steel P of Comparative Example is lower than 7 in the grain size number and cannot meet the above equations Eq. (1) and Eq. (3), and therefore low in impact strength. The gear specimen formed of the steel Q is lower than 7 in the grain size number and cannot meet the above equations Eq. (2) and Eq. (3), and therefore is low in impact strength.

EXPERIMENT 2

**[0046]** Steels 1 to 3 of Examples (according to the present invention) and steels 4 to 9 of Comparative Examples (not according to the present invention) in an amount of 150 Kg were produced in a usual manner under vacuum melting. The steels A to R and the steels N to Q had chemical compositions shown in Table 3. The steels 1 to 3 met all the equations Eq. (1), Eq. (3) and Eq. (4), whereas the steels 4 to 9 cannot meet at least one of the equations Eq. (1), Eq. (3) and Eq. (4). The steel 8 of Comparative Example corresponded to a conventional case hardening steel identified as SCM418H according to JIS.

**[0047]** Subsequently, each of the steels of Examples and Comparative Examples was subjected to rolling in a usual manner and formed into a bar material, and thereafter underwent cutting, spheroidizing annealing, shot blasting, a treatment for forming lubricating coating, and cold teeth forging. Thereafter, the bar material was subjected to cutting such as turning or the like so as to be formed into a gear of the final shape as shown in Fig. 5A. The bar material might be formed into the final shape of a gear as shown in 5B. The gear of the final shape was then subjected to carburizing hardening and tempering, followed by finish grinding, thereby obtaining a gear specimen of each of the steels 1 to 3 of Examples and the steels 4 to 9 of Comparative Examples, as shown in Fig. 5A.

**[0048]** The gear of the final shape shown in Fig. 5A or 5B may be produced by another production method in which the steel is formed into a certain blank shape under cold forging and thereafter subjected to turning and gear cutting. Concerning the steels 1 to 3 of Examples, forming of the gear may be sufficiently accomplished even if the spheroidizing annealing as a softening heat treatment made before the cold forging is omitted.

**[0049]** The impact test was conducted on each of the gear specimens of the steels 1 to 3 of Examples and steels 4 to 9 of Comparative Examples by using the drop impact tester in the same manner as that for the gear specimens in Experiment 1, in which the 100 times impact strength was measured for each gear specimen. Then, calculation was made for each gear specimen to determine a ratio of the 100 times impact strength of each gear specimen to the 100 times impact strength of the gear specimen of the steel 8 of Comparative Example (corresponding to the case hardening steel SCM418H according to JIS) on the assumption that the 100 times impact strength of the steel 8 was 100. This ratio was referred to as "100 times impact strength ratio" and shown in Table 4.

**[0050]** Additionally, in order to determine cold forgeability of each of the gear specimens of the steels 1 to 3 of Examples and the gear specimens of the steels 4 to 9 of Comparative Examples, a press load (or cold forging load) applied to the base material for each gear specimen was measured during the above cold teeth forging by using a load cell equipped with a press work machine. It will be understood that the cold forgeability is excellent as the press load is low. Then, calculation was made for each gear specimen to determine a ratio of the press load of each gear specimen to the press load of the gear specimen of the steel 8 of Comparative Example (corresponding to the case hardening steel SCM418H according to JIS) on the assumption that press load of the steel 8 was 100. This ratio was referred to as "cold forging load ratio" and shown in Table 4. Furthermore, each of the gear specimens of the steels 1 to 3 of Examples and the steels 4 to 9 of Comparative Examples was subjected to measurement of Rockwell hardness (B-scale). The measured Rockwell hardness (HRB) of the gear specimens were shown in Table 4.

**[0051]** As apparent from the experimental results shown in Table 4, it is confirmed that the steels 1 to 3 of Examples meet the equations Eq. (1), Eq. (3) and Eq. (4) and therefore are excellent both in cold forgeability and impact strength. In contrast, it is confirmed that the steels 4, 5 and 9 of Comparative Examples meet the equations Eq. (1) and Eq. (3) and therefore excellent in impact strength; however, they cannot meet the equation Eq. (4) and therefore are inferior in cold forgeability. The steels 7 and 8 of Comparative Examples meet the equations Eq. (1) and Eq. (4) and cannot meet the equation Eq. (3), and therefore are inferior in impact strength.

**[0052]** While the present invention has been discussed particularly on examples of gears, it will be appreciated that the principle of the present invention may be applied to all machinery structural parts in which impact strength is particularly regarded as important.

**[0053]** As appreciated from the above, according to the present invention, the amounts of elements of C, Mn, Mo, P and S inherently contained in case hardening steel and of B and the like are controlled within specified content ranges thereby establishing a suitable balance between crystal grain size and a carburized case (hardened layer). This can provide the case hardening steel high in impact strength without large increase in material cost and processing cost, and the carburized part using the thus improved case hardening steel.

**[0054]** The entire contents of Japanese Patent Applications P2001-216990 (filed July 17, 2001) and P2002-075624 (filed March 19, 2002) are incorporated herein by reference.

**[0055]** Although the invention has been described above by reference to certain embodiments and examples of the invention, the invention is not limited to the embodiments and examples described above. Modifications and variations of the embodiments and examples described above will occur to those skilled in the art, in light of the above teachings. The scope of the invention is defined with reference to the appended claims.

# TABLE 1

| | | C | Si | Mn | P | S | Cr | Mo | B | Al | N | Nb | Ti | Pb | Bi | Ca |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloy of Example | A | 0.18 | 0.20 | 1.45 | 0.008 | 0.009 | - | 0.15 | - | 0.030 | 0.012 | - | - | - | - | - |
| | B | 0.19 | 0.25 | 0.74 | 0.007 | 0.006 | 1.01 | - | - | 0.029 | 0.013 | - | - | - | - | - |
| | C | 0.19 | 0.31 | 1.47 | 0.010 | 0.008 | - | 0.25 | - | 0.029 | 0.011 | - | - | - | - | - |
| | D | 0.20 | 0.43 | 0.71 | 0.007 | 0.008 | 1.03 | - | - | 0.030 | 0.013 | - | - | - | - | - |
| | E | 0.18 | 0.08 | 0.50 | 0.009 | 0.006 | 1.48 | - | - | 0.031 | 0.012 | - | - | - | - | - |
| | F | 0.18 | 0.06 | 0.50 | 0.009 | 0.010 | 1.47 | - | 0.0018 | 0.029 | 0.008 | 0.090 | 0.033 | - | - | - |
| | G | 0.18 | 0.10 | 0.65 | 0.011 | 0.017 | 0.96 | 0.40 | 0.0018 | 0.034 | 0.007 | 0.046 | 0.035 | - | - | - |
| | H | 0.19 | 0.07 | 0.30 | 0.012 | 0.015 | 0.30 | 0.75 | 0.0019 | 0.032 | 0.008 | 0.051 | 0.037 | - | - | - |
| | I | 0.18 | 0.06 | 1.48 | 0.011 | 0.015 | 1.12 | 0.00 | 0.0014 | 0.033 | 0.007 | 0.070 | 0.040 | - | - | - |
| | K | 0.18 | 0.09 | 0.48 | 0.007 | 0.012 | 1.00 | 0.41 | 0.0015 | 0.030 | 0.009 | 0.050 | 0.028 | 0.09 | - | - |
| | L | 0.18 | 0.09 | 0.49 | 0.009 | 0.011 | 1.03 | 0.41 | 0.0015 | 0.029 | 0.009 | 0.034 | 0.036 | - | 0.07 | - |
| | M | 0.19 | 0.10 | 0.47 | 0.009 | 0.012 | 1.02 | 0.40 | - | 0.029 | 0.010 | - | - | - | - | 0.03 |
| | R | 0.20 | 0.23 | 0.90 | 0.008 | 0.007 | - | - | - | 0.032 | 0.011 | - | - | - | - | - |
| Alloy of Compr. Example | N | 0.21 | 0.20 | 0.76 | 0.023 | 0.015 | 1.11 | - | - | 0.032 | 0.012 | - | - | - | - | - |
| | O | 0.18 | 0.43 | 0.35 | 0.011 | 0.017 | 2.62 | - | - | 0.033 | 0.009 | - | - | - | - | - |
| | P | 0.19 | 0.07 | 0.83 | 0.020 | 0.020 | 1.08 | 0.35 | - | - | - | - | - | - | - | - |
| | Q | 0.18 | 0.06 | 0.50 | 0.011 | 0.014 | 1.47 | - | 0.0013 | 0.029 | 0.008 | - | - | - | - | - |

TABLE 2

| | | Austenite grain size | (left side)-(right side) of Eq. (1) | (left side)-(right side) of Eq. (2) | 100 times impact strength (Nm) |
|---|---|---|---|---|---|
| Alloy of Example | A | 8.0 | (1)-0.160 | -0.049 | 12663 |
| | B | 7.5 | (2)-0.063 | -0.016 | 12518 |
| | C | 8.1 | (1)-0.160 | -0.040 | 12653 |
| | D | 8.3 | (2)-0.039 | -0.002 | 12397 |
| | E | 9.1 | (2)-0.033 | -0.019 | 12454 |
| | F | 8.9 | (2)-0.013 | -0.170 | 13123 |
| | G | 8.8 | (1)-0.036 | -0.147 | 12813 |
| | H | 11.0 | (1)-0.031 | -0.172 | 13024 |
| | I | 9.4 | (1)-0.100 | -0.144 | 13008 |
| | K | 8.3 | (1)-0.061 | -0.153 | 13001 |
| | L | 9.0 | (1)-0.058 | -0.155 | 13017 |
| | M | 9.5 | (1)-0.039 | -0.133 | 12939 |
| | R | 9.0 | (2)-0.063 | -0.017 | 12530 |
| Alloy of Compr. Example | N | 8.4 | (2)-0.080 | 0.125 | 11917 |
| | O | 8.0 | (2)-0.051 | 0.065 | 12134 |
| | P | 5.1 | (1)-0.018 | 0.126 | 11914 |
| | Q | 4.3 | (2)-0.070 | 0.000 | 12289 |
| Eq. (1) : [C%] + 5[P%+S%] ≦ ([Mn%] + [Mo%] + 1.8) / 8<br>Eq. (2) : [C%] + 5.2[P%+S%] ≦ ([Mn%] + [Mo%] + 3.8) / 22 + 96[B%] + [JIS austenite grain size number] /111 | | | | | |

TABLE 3

| | | C | Si | Mn | P | S | Cr | Mo | B | Nb |
|---|---|---|---|---|---|---|---|---|---|---|
| Alloy of Example | 1 | 0.19 | 0.07 | 0.41 | 0.006 | 0.017 | 0.97 | 0.15 | 0.0014 | 0.05 |
| | 2 | 0.18 | 0.05 | 0.74 | 0.007 | 0.012 | 1.09 | 0.01 | 0.0017 | 0.05 |
| | 3 | 0.18 | 0.10 | 0.50 | 0.010 | 0.018 | 1.00 | 0.20 | 0.0015 | 0.05 |
| Alloy of Compr. Example | 4 | 0.17 | 0.07 | 0.59 | 0.010 | 0.017 | 0.92 | 0.41 | 0.0013 | 0.05 |
| | 5 | 0.18 | 0.07 | 0.40 | 0.008 | 0.015 | 0.95 | 0.40 | 0.0015 | 0.05 |
| | 6 | 0.19 | 0.07 | 1.44 | 0.009 | 0.015 | 0.97 | 0.00 | - | 0.00 |
| | 7 | 0.19 | 0.06 | 0.82 | 0.008 | 0.014 | 1.07 | 0.41 | - | 0.00 |
| | 8 | 0.19 | 0.19 | 0.79 | 0.013 | 0.017 | 0.97 | 0.16 | - | 0.00 |
| | 9 | 0.21 | 0.15 | 0.60 | 0.015 | 0.020 | 1.20 | 0.25 | 0.0030 | 0.07 |

# TABLE 4

| | | Cold forgeability | | | Impact strength | | | |
|---|---|---|---|---|---|---|---|---|
| | | Left side of Eq. (4) | Hardness (HRB) | Cold forging load ratio | (left side)-(right side) of Eq. (1) | (left side)-(right side) of Eq. (3) | 100 times impact strength ratio | Austenite grain size |
| Alloy of Example | 1 | 33.4 | 74 | 100 | -0.220 | -0.095 | 124 | 7.99 |
| | 2 | 35.1 | 73 | 98 | -0.234 | -0.163 | 128 | 7.97 |
| | 3 | 39.6 | 79 | 104 | -0.273 | -0.095 | 124 | 8.00 |
| Alloy of Compr. Example | 4 | 46.3 | 85 | 117 | -0.315 | -0.105 | 126 | 8.04 |
| | 5 | 41.4 | 82 | 109 | -0.260 | -0.126 | 123 | 8.05 |
| | 6 | 40.2 | 81 | 105 | -0.335 | 0.005 | 110 | 7.95 |
| | 7 | 38.0 | 77 | 102 | -0.299 | 0.004 | 108 | 7.97 |
| | 8 | 39.4 | 79 | 100 | -0.304 | 0.058 | 100 | 8.00 |
| | 9 | 47.7 | 88 | 117 | -0.296 | -0.179 | 130 | 7.95 |

Eq. (1) : $[C\%] + 5[P\%+S\%] \leqq ([Mn\%] + [Mo\%] + 1.8) / 8$

Eq. (3) : $[C\%] + 5.2[P\%+S\%] \leqq ([Mn\%] + [Mo\%] + 3.8) / 22 + 96[B] + [\text{JIS grain size number}] / 111$

Eq. (4) : $80[Si\%] + 24[Mn\%] + 33[Mo\%] + 13) \leqq 40$

## Claims

1. A case hardening steel consisting essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of from more than 0.3 to 1.0 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight,

phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, molybdenum in an amount of not more than 1.0 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, and balance being iron and inevitable impurities,

wherein said case hardening steel meets the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + [Mo\ \%] + 1.8) / 8 \qquad \text{Eq. (1).}$$

2. A case hardening steel consisting essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of from more than 0.3 to 1.0 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, chromium in an amount of from more than 0 to 1.6 % by weight, and balance being iron (Fe) and inevitable impurities,

wherein the case hardening steel meets the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + 1.8) / 8 \qquad \text{Eq. (2).}$$

3. A case hardening steel consisting essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of not more than 0.3 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, molybdenum in an amount of not more than 1.0 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, and balance being iron and inevitable impurities,

wherein said case hardening steel meets the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + [Mo\ \%] + 1.8) / 8 \qquad \text{Eq. (1).}$$

4. A case hardening steel consisting essentially of carbon in an amount of from 0.1 to 0.3 % by weight, silicon in an amount of not more than 0.3 % by weight, manganese in an amount of from 0.3 to 1.7 % by weight, phosphorus in an amount of not more than 0.03 % by weight, sulfur in an amount of not more than 0.03 % by weight, aluminum in an amount of not more than 0.04 % by weight, nitrogen in an amount of not more than 0.03 % by weight, and balance being iron and inevitable impurities,

wherein the case hardening steel meets the following equation:

$$[C\ \%] + 5([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + 1.8) / 8 \qquad \text{Eq. (2).}$$

5. A case hardening steel as claimed in Claim 3 or 4, further consisting essentially of chromium in an amount of from more than 0 to 1.6 % by weight.

6. A case hardening steel as claimed in any of Claims 1 to 5, further consisting essentially of boron in an amount of from 0.001 to 0.005 % by weight, and at lease one of niobium in an amount of from 0.01 to 0.10 % by weight and titanium in an amount of from 0.01 to 0.10 % by weight.

7. A case hardening steel as claimed in any of Claims 1 to 6, wherein said case hardening steel has an elemental composition to meet the following equation:

$$[C\ \%] + 5.2\ ([P\ \%] + [S\ \%]) \leq ([Mn\ \%] + [Mo\ \%] + 3.8) / 22 +$$

$$96\ [B\ \%] + [\text{austenite grain size number according to JIS G 0551}] / 111 \qquad \text{Eq. (3)}$$

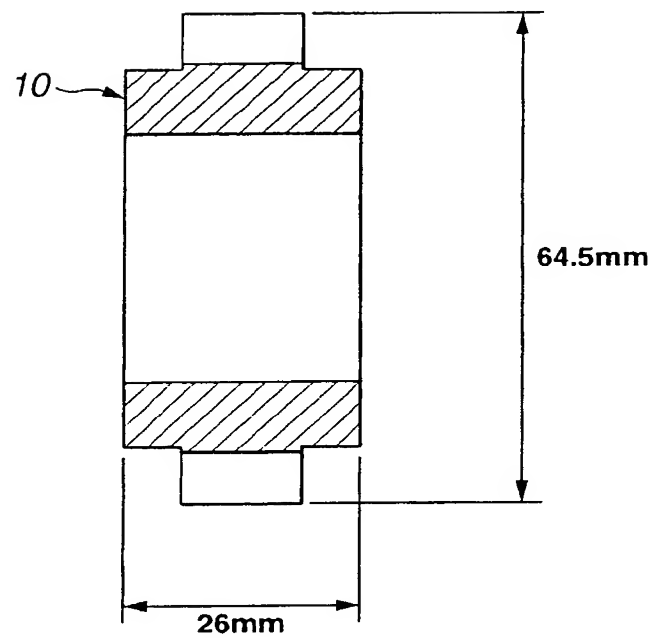
8. A case hardening steel as claimed in any of Claims 3 to 7,
wherein said case hardening steel has an elemental composition to meet the following equation:

$$80\,[Si\,\%] + 24\,[Mn\,\%] + 33\,[Mo\,\%] + 13 \leq 40 \qquad \text{Eq. (4)}$$

9. A case hardening steel as claimed in any of Claims 1 to 8, further consisting essentially of at least one selected from the group consisting of lead in an amount of not more than 0.3 % by weight, bismuth in an amount of not more than 0.15 % by weight and calcium in an amount of not more than 0.1 % by weight.

10. A carburized part formed of a case hardening steel as claimed in any of Claims 1 to 9, wherein said carburized part has a hardened layer of carburized case including fine austenite whose austenite grain size number according to JIS G 0551 is not smaller than 7.

# FIG.1




# FIG.2

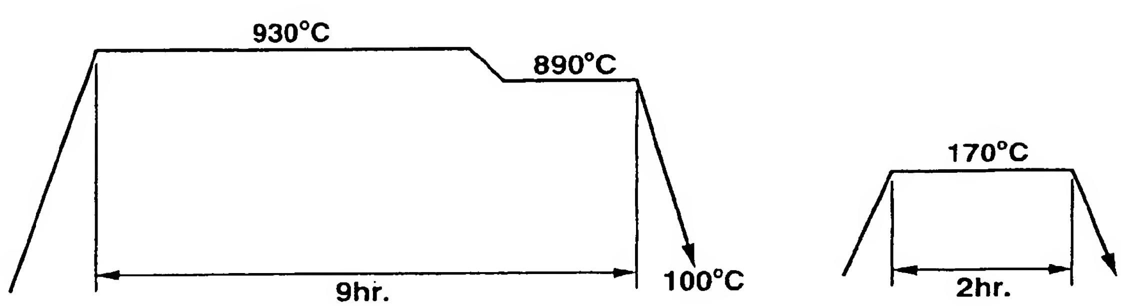


FIG.3

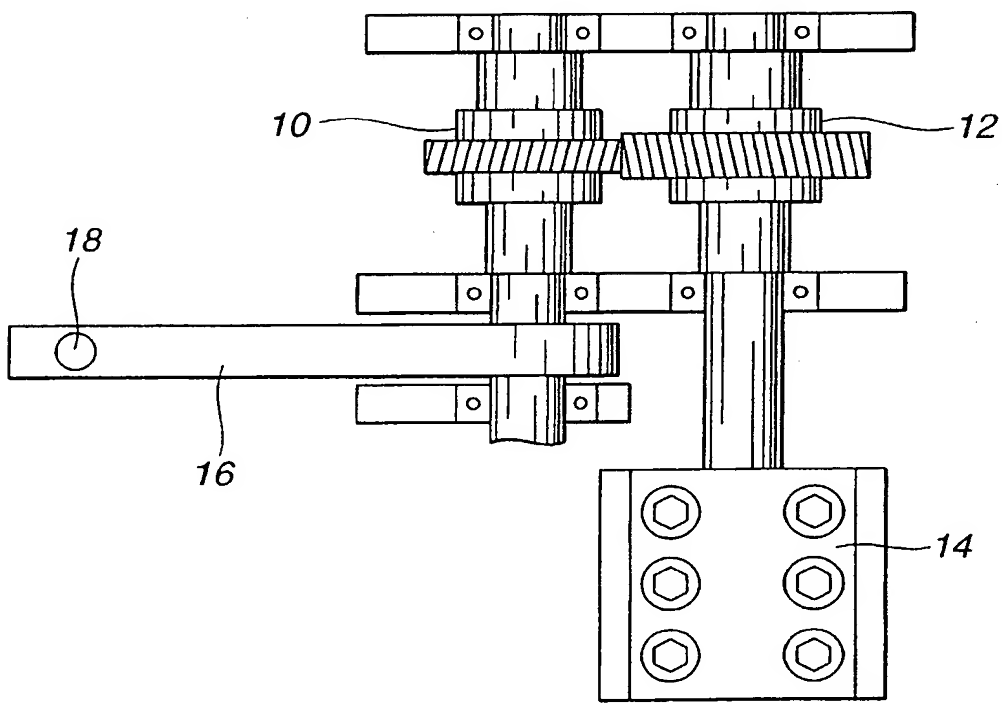


FIG.4

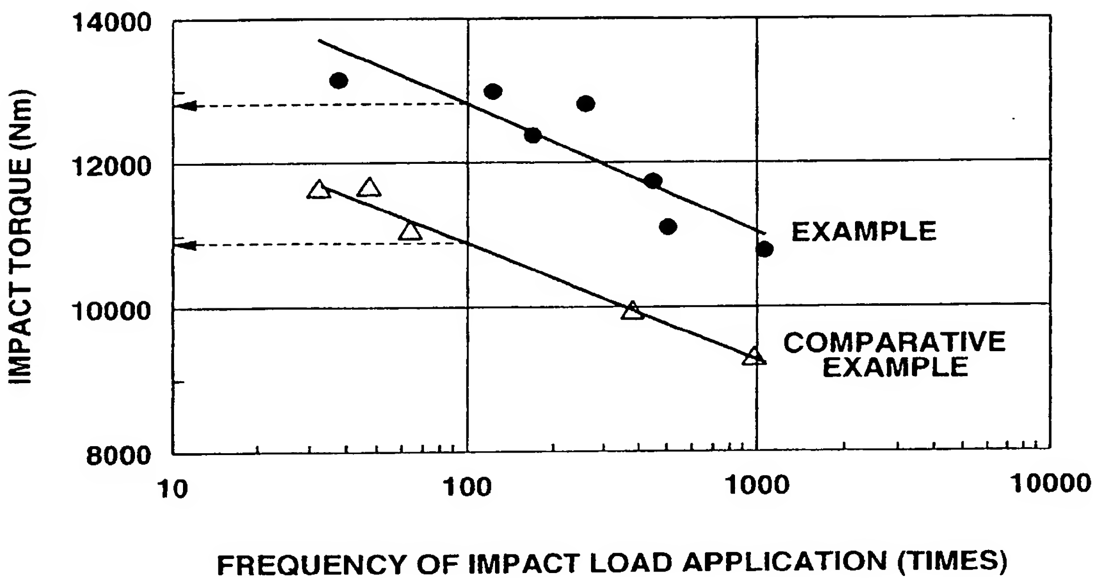



FIG.5A

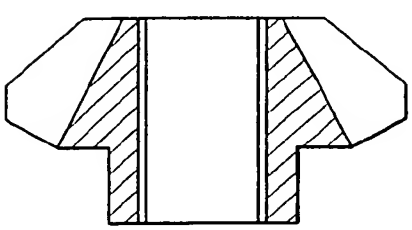
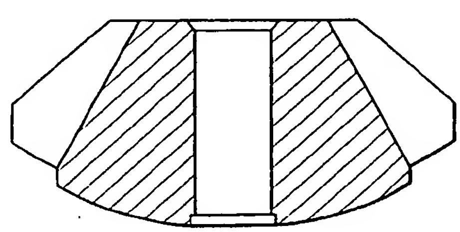
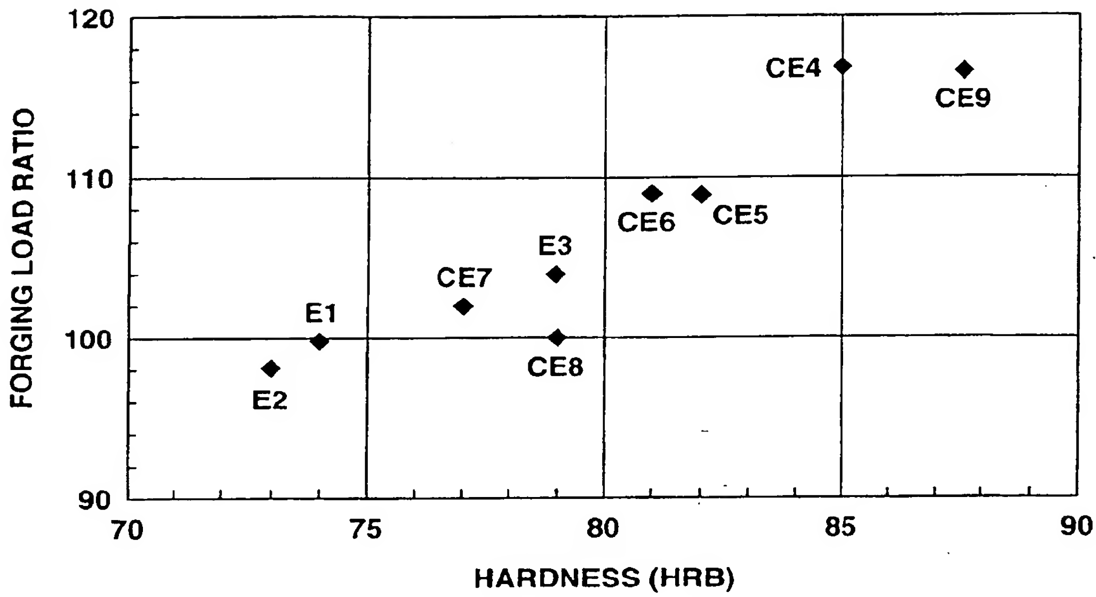


FIG.5B

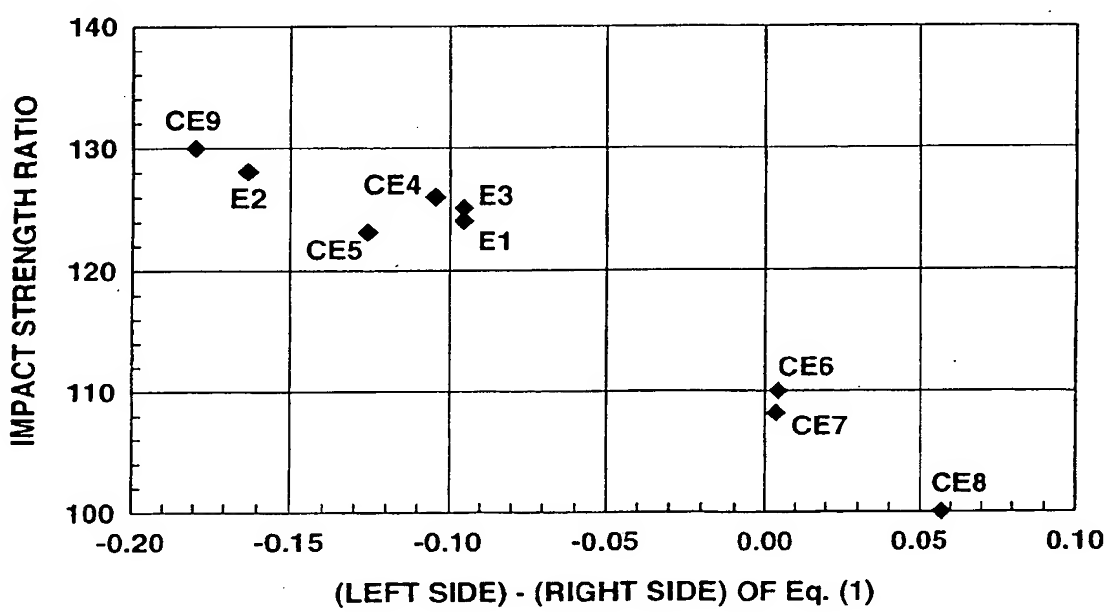


# FIG.6



FORGING LOAD RATIO
HARDNESS (HRB)
120
110
100
90
70
75
80
85
90
CE4
CE9
CE6
CE5
E3
CE7
E1
CE8
E2


# FIG.7



IMPACT STRENGTH RATIO
(LEFT SIDE) - (RIGHT SIDE) OF Eq. (1)
140
130
120
110
100
-0.20
-0.15
-0.10
-0.05
0.00
0.05
0.10
CE9
E2
CE4
E3
E1
CE5
CE6
CE7
CE8

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 02 01 5081

| Category | DOCUMENTS CONSIDERED TO BE RELEVANT<br>Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
|---|---|---|---|
| X | US 4 802 918 A (OOKI TAKAO ET AL)<br>7 February 1989 (1989-02-07)<br>* claim 1; table 1 * | 1-10 | C22C38/00<br>C22C38/02<br>C22C38/04<br>C23C8/26 |
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 012, no. 496 (C-555),<br>23 December 1988 (1988-12-23)<br>-& JP 63 206449 A (KOBE STEEL LTD),<br>25 August 1988 (1988-08-25)<br>* abstract; examples A,B; table 1 * | 3-10 | |
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 1995, no. 11,<br>26 December 1995 (1995-12-26)<br>-& JP 07 207423 A (NIPPON STEEL CORP),<br>8 August 1995 (1995-08-08)<br>* abstract; example E; table 3 * | 3-10 | |
| A,D | PATENT ABSTRACTS OF JAPAN<br>vol. 1997, no. 12,<br>25 December 1997 (1997-12-25)<br>-& JP 09 201644 A (NISSAN MOTOR CO LTD),<br>5 August 1997 (1997-08-05)<br>* abstract * | 1-10 | TECHNICAL FIELDS SEARCHED (Int.Cl.7)<br>C22C<br>C23C |
| A | US 4 634 573 A (YANAGIYA TOSHIO ET AL)<br>6 January 1987 (1987-01-06)<br>* the whole document * | 1-10 | |
| A | FR 2 339 678 A (UGINE ACIERS)<br>26 August 1977 (1977-08-26)<br>* the whole document * | 6 | |
| A | EDITED BY J. R. DAVIS: "Carbon and Alloy Steels"<br>March 1996 (1996-03) , ASM INTERNATIONAL , USA XP002214993<br>* page 159 - page 162 * | 1-10 | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| MUNICH | 27 September 2002 | Swiatek, R |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03 82 (P04C01)

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 02 01 5081

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

27-09-2002

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 4802918 A | 07-02-1989 | JP 1868815 C | 06-09-1994 |
| | | JP 5079745 B | 04-11-1993 |
| | | JP 62054064 A | 09-03-1987 |
| | | DE 3685816 D1 | 30-07-1992 |
| | | DE 3685816 T4 | 10-02-1994 |
| | | EP 0236505 A1 | 16-09-1987 |
| | | WO 8701396 A1 | 12-03-1987 |
| JP 63206449 A | 25-08-1988 | JP 1868867 C | 06-09-1994 |
| | | JP 5063542 B | 10-09-1993 |
| JP 07207423 A | 08-08-1995 | NONE | |
| JP 09201644 A | 05-08-1997 | NONE | |
| US 4634573 A | 06-01-1987 | JP 1749416 C | 08-04-1993 |
| | | JP 3007744 B | 04-02-1991 |
| | | JP 58045354 A | 16-03-1983 |
| FR 2339678 A | 26-08-1977 | FR 2339678 A1 | 26-08-1977 |
| | | BE 850831 A1 | 28-07-1977 |
| | | CH 619270 A5 | 15-09-1980 |
| | | DE 2703149 A1 | 04-08-1977 |
| | | ES 455347 A1 | 16-01-1978 |
| | | IN 147052 A1 | 27-10-1979 |
| | | IT 1075064 B | 22-04-1985 |
| | | LU 76646 A1 | 03-08-1977 |
| | | NL 7700957 A | 01-08-1977 |

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82